"Characterization of Water Soluble Polymers"

Final Report (1982-1983 Project Year)

Prepared for Energy Mines & Resources Canada

Contract #015G 23440-2-9150

Serial No. 0SG82-00065

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MICROMEDIA

15 pp

November 1, 1983

In this final report we are presenting QELS (Quasi Elastic Laser light-scattering) measurements which were carried out to characterize the polyacrylamide and polyethylene oxide flocullants. However due to an increasing interest in polyacrylamide, expressed by the scientific authority a major portion of this work is primary devoted to the study of this polymer. These flocullants were obtained from Polysciences Inc., Warrington, Pennsylvania. The techniques of data acquisition and analysis are similar to that reported in report #1 on the first phase of this work.

The present report summarizes some of the preliminary study on the polyacrylamide model system and still requires more experiments over a wide range of molecular weights to corroborate established models or to develop new ones. Furthermore a detailed analysis of data is needed to study the interactions in the solution. These will be accomplished during the second term of the project. The following report is divided into two parts:

A. Size analysis:

In the first part of this work QELS experiments were performed on samples of polyacrylamide and polyethylene oxide solutions in the concentration range of ~ 5 mg/ml – 20 mg/ml, as a function of varying scattering angle. The data was analyzed by both cumulant analysis and the exponential sampling method, that of plotting histograms. Both of these techniques were discussed in an earlier report. These experiments were also carried out as a function of time in terms of a few hours, days to a few weeks. We did not find sufficient evidence of polymer degradation during this period. However, most of the experiments were completed within 24 hours of sample preparation. Our measurements have been found to be reproducible and consistent with earlier measurements. The measurements were time consuming and difficult because of the following reasons:

i) The presence of dust in the sample.

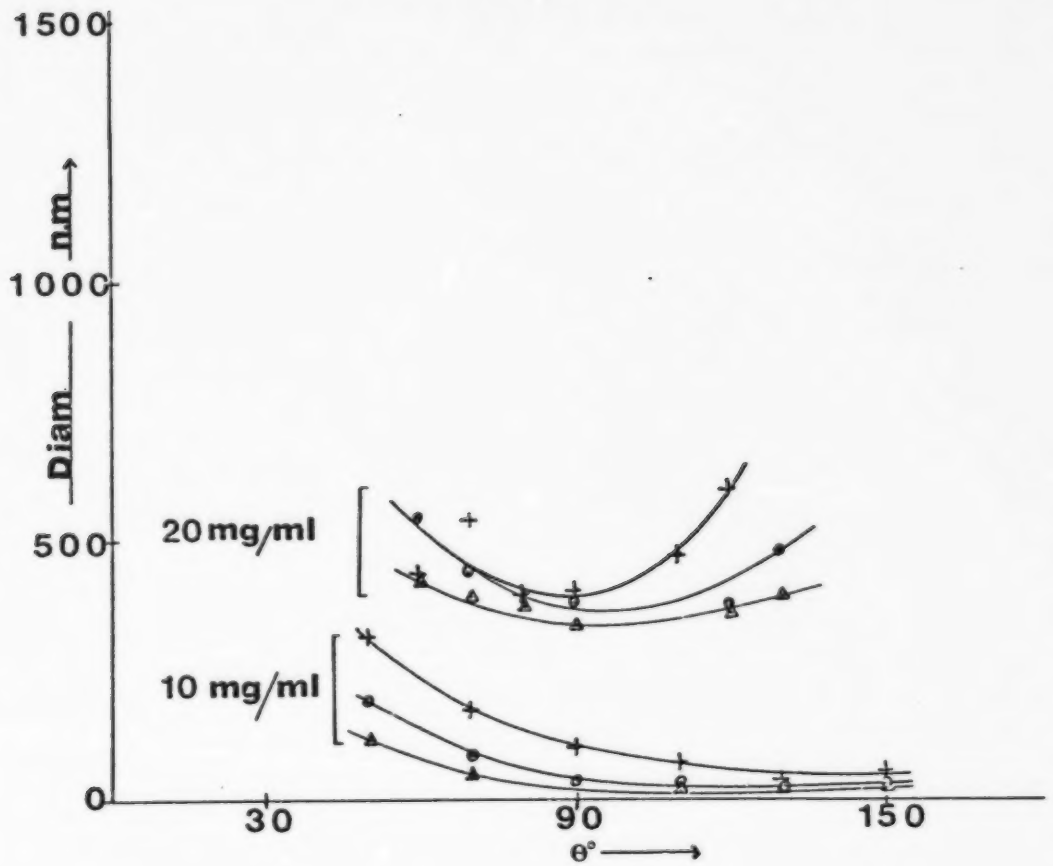


Figure #1: Size profiles:

The sizes of polyacrylamide flocullants for two separate concentrations as a function of scattering angle θ. The methods of cumulant was adopted to extract floc diameter in nanometers from QELS data. Each set of curves is plotted at three different bin times τ_1, τ_2 and τ_3 such that $\tau_1 < \tau_2 < \tau_3$.

ii) The polydispersity of the sample.

The removal of dust was achieved through standard technique of centrifugation. The rate of centrifugation was found to be critically dependent on sample concentration. A slight change in the rate of centrifugation results in polymer coagulation which traps the dust and yield a polymer gel. The viscosities of the samples were determined by rotating drum method (RDM).

The QELS measurement on our model system is found to be dependent on the experiment run time. Small run times ~ 5 to 10 minutes, which is more than sufficient in case of polystyrene latex spheres, is in fact barely enough. This can be attributed to the greater polydispersity present in the sample. The slow component (long time fluctuations) in the sample does not yield a satisfactory count rate for the correlator to build the correlation function. Henceforth the signal to noise ratio at short run times is greatly reduced. We alleviated these problems by increasing the run time to two hours for these measurements. This enhances the signal to noise ratio, greatly, improves the counting statistics, and yields good reproducible correlation functions. An alternate way to handle this problem would be to increase the aperture of the quantum photometer and modify the coherence conditions by modifying the collecting optics. Furthermore the scattered intensity was found to be decreasing in the direction of increasing scattering angle θ. This can be attributed to the presence of large particles. Hence the measurements can be performed in the back scattering mode. However both these newer methods were not tried in the present study. Typical of these measurements is the Polyacrylamide system. Size measurements are presented in figures 1 and 2. These curves present

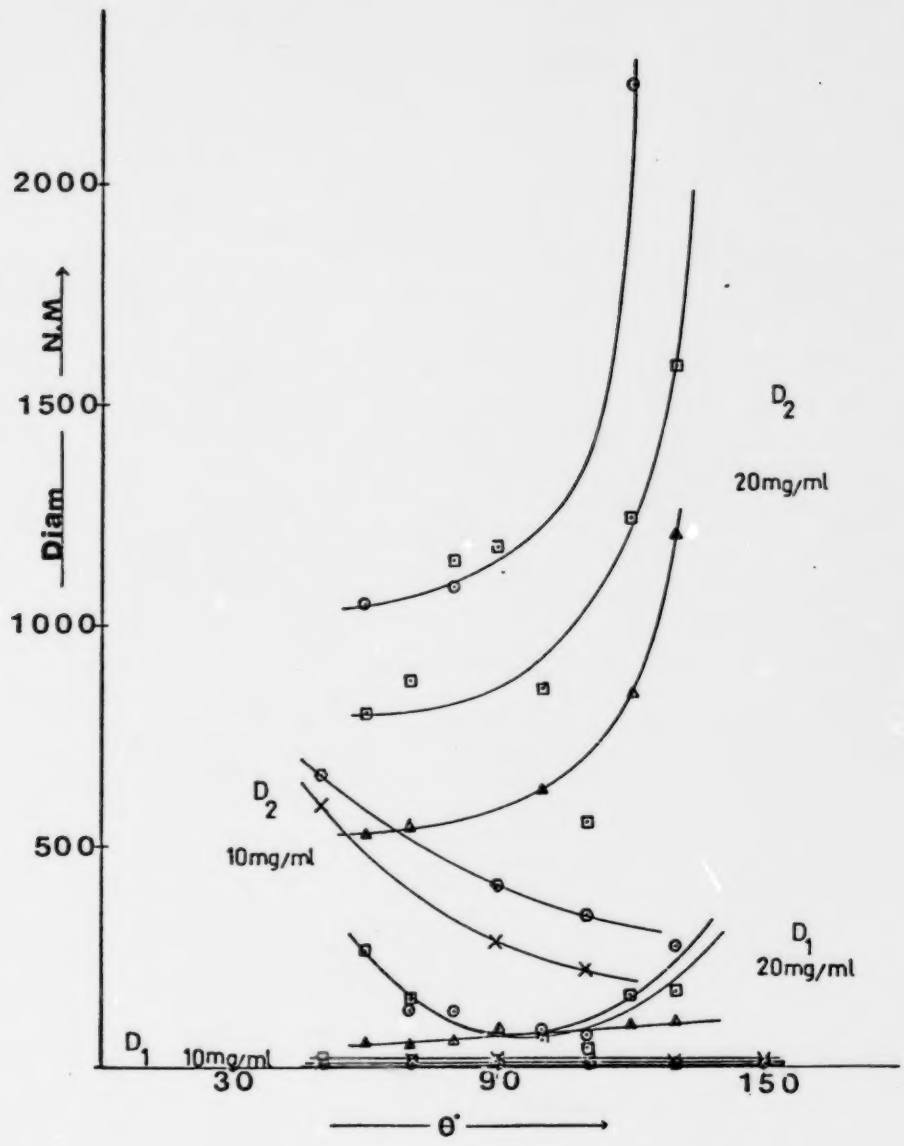


Figure #2: Size profiles:

The sizes of polyacrylamide flocullants for two separate concentrations was obtained by employing the technique of two exponentials. D_1 and D_2 represents the two relaxing components of polyacrylamide system. QELS measurements as a function of scattering angle θ and floc, concentration clearly indicate the systems polydispersity. The sizes in terms of the diameter is presented in nanometers. Each set of curves represents a measurement at bin times of τ_1, τ_2 and τ_3.

measurements on three different bin time (τ_1, τ_2, τ_3). The sizes were obtained by cumulant method. Lower set of curves is for a flocullant concentration of 10 mg/ml and the upper set is for 20 mg/ml. These curves clearly indicate a strong concentration dependence, angular dependence, and sampling time dependence which provides an evidence of the high polydispersity of the model system.

Figure 2 summarizes the size analysis as a function of concentration and an angular variation, employing two exponential method. The lowest set of three curves at the bottom is for 10 mg/ml concentration showing no angular dependence on $D_1(\tau_1)$, $D_1(\tau_2)$, and $D_1(\tau_3)$ i.e the diameters obtained at the different bin times τ_1, τ_2, and τ_3. D_1's are the diameters obtained by the relaxation of the first exponential component. (Eqn. 8 Report 1) The next set of curves is for 20 mg/ml concentration, showing a strong θ dependence on D_1's at three different τ's. Similarly the slow component i.e. D_2 for 10 mg/ml and 20 mg/ml is shown in the upper two sets of curves, showing strong concentration and θ dependence.

In summary what we achieved at the end of these measurements is a profile of size distribution.

B. Labelling Experiments:

In order to better characterize the flocullant system completely we needed more information. We did get a tentative profile of size distribution from the experiments mentioned above but did not get any information about the shape, the nature of the flocullant i.e. whether it is a free draining or non free draining random coil and the extent of interactions like hydrodynamic or electrostatic interactions, and a dependence of these factors on molecular weights. We have also seen that

the experiments are difficult in obtaining data or even reprodoucible results due to the pesence of dust in the polymer itself and even at very high concentration ($\simeq$ 20 mg/ml) the problem of low scattered intensity. Therefore for these reasons we carried out "labelling" experiment on two samples of polyacrylamide of molecular weight 500,000 (5×10^5) and one million (10^6). These labelling experiments circumvented many difficulties encountered in the study presented in part A. The measurements also indicate that the diffusion ratio, D/D_o, of labelling spheres is dependent upon the polacrylamide molecular weight. The labels were provided by utilizing polystrene latex spheres of 0.109 μ diameter. This technique of hindered diffusion is described by D. N. Turner and F. R. Hallett. A sphere concentration of 3×10^6 spheres per ml was utilized, in a matrix of polymer solution. This matrix was adjusted in an approximate way to yield 95% of light scattered by diffusing latex spheres. The diffusion coefficient of the spheres D can be related to the volume fraction ϕ of the polyacrylamide:

$$\frac{D}{D_o} = 1/(1 + \nu\phi + k\phi^2) \qquad (1)$$

where ν is the Simha's shape parameter, ϕ is the volume fraction and k is the interaction parameter. D_o is the diffusion coeff. of spheres in zero polyacrylamide concentration. The experiments were performed at a fixed angle of 90^o, as a fn. of varying concentration. Typical results are shown in figure 3 and 4 which shows that the varying polyacrylamide concentration effects the labelling spheres diffusion coefficient. Following this experiment, few more experiments were conducted to check the reproducibility of our measurements. The new experiments verified our previous measurements and the data was found to be reproducible within experimental limitations.

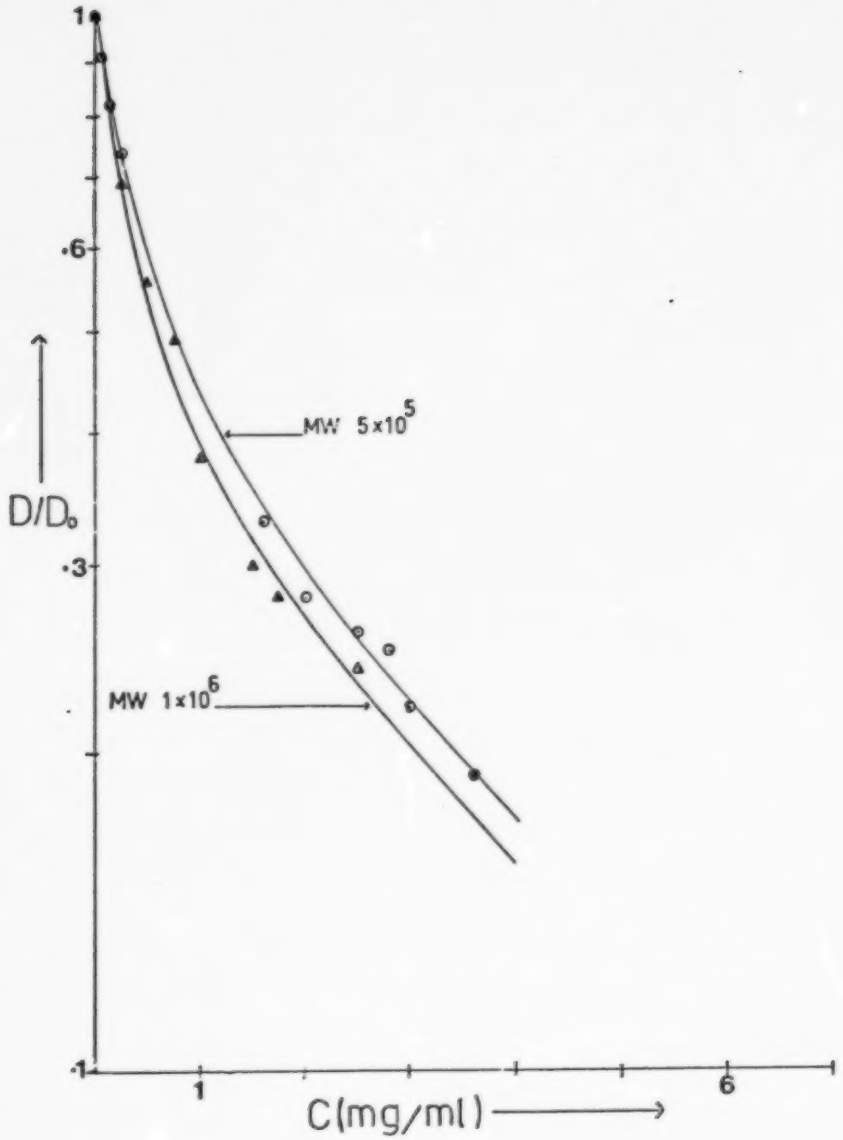


Figure #3: Labelling experiment:

The diffusion ratio of labels as a function of polyacrylamide concentration. The labels were provided by diffusing polystyrene latex spheres of 0.109 µm diameter through the polyacrylamide matrix. D_o is the diffusion coefficient of spheres at zero polymer concentration . It clearly indicates that diffusion is sensitive to molecular weight of the polyacrylamide.

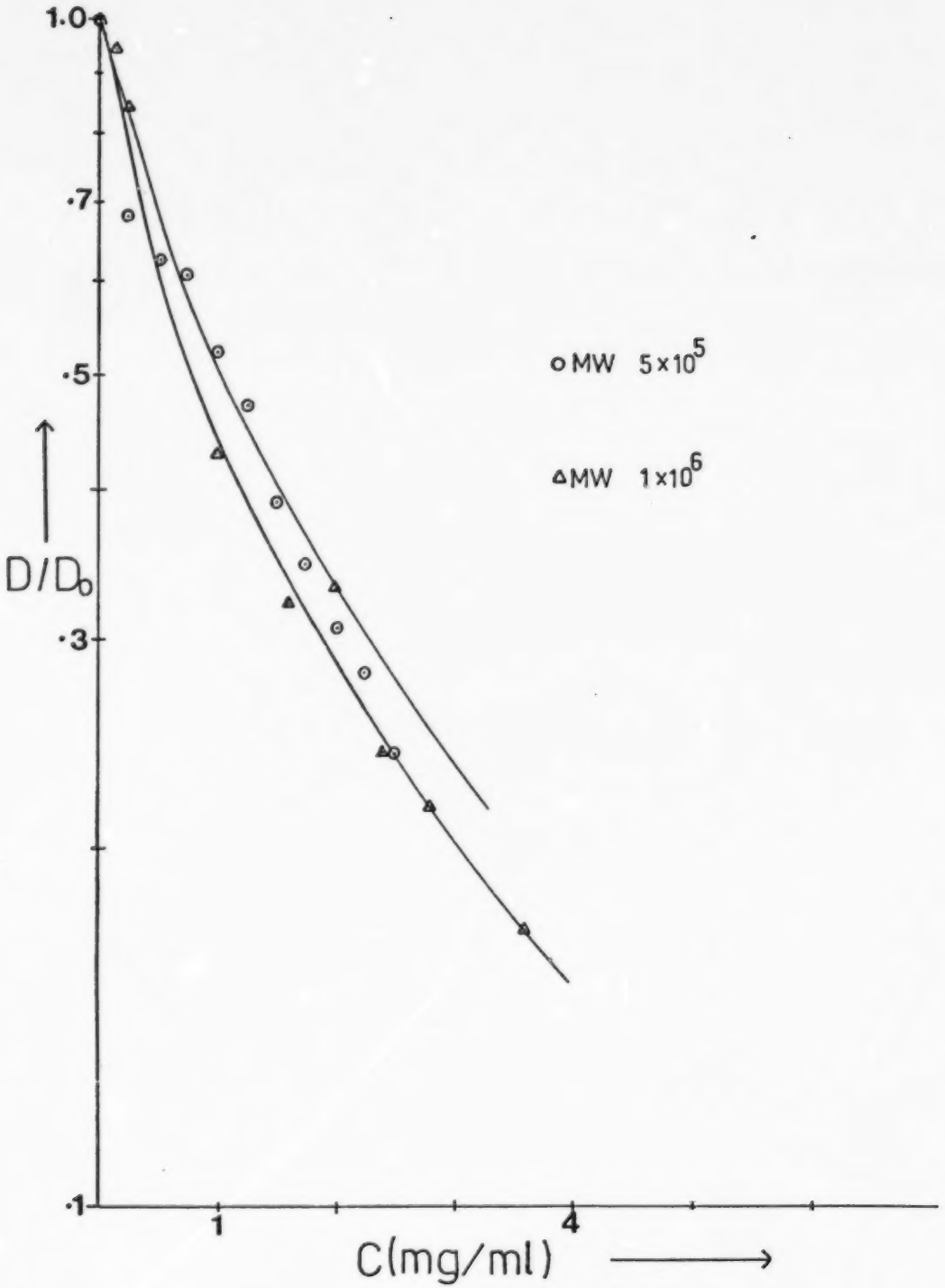


Figure #4: Labelling experiment:

This experiment is similar to that of figure 3. It was performed to check the reproducibility of experiment reported in figure 3.

These measurements clearly indicate the extent of interactions and changes in confirmation in the Polyacrylamide matrix as we go from lower to higher polymer concentration. A careful analysis of this data can provide information on intrinsic viscosity [η], mol. wt, radius of gyration, characteristic ratio, relative scattered intensity of translational mode and molecular weight distributions. Intrinsic visocity [η] is an important parameter as it can be helpful in deducing other physical parameters such as radius of gyration and characteristic ratio. Since the QELS experiments provide diffusion ratio D/D_o, this can be related to the viscosity because

$$D/D_o = \eta_o/\eta \qquad (2)$$

The intrinsic visocity [η] then is given by

$$[\eta] = \lim_{c \to o} \frac{\eta - \eta_o}{\eta_o c} \equiv \lim_{c \to o} \frac{\eta_{sp}}{c} \qquad (3)$$

where η is the solution viscosity,

η_o is the viscosity of pure solvent

η_{sp} is the sp. viscosity and

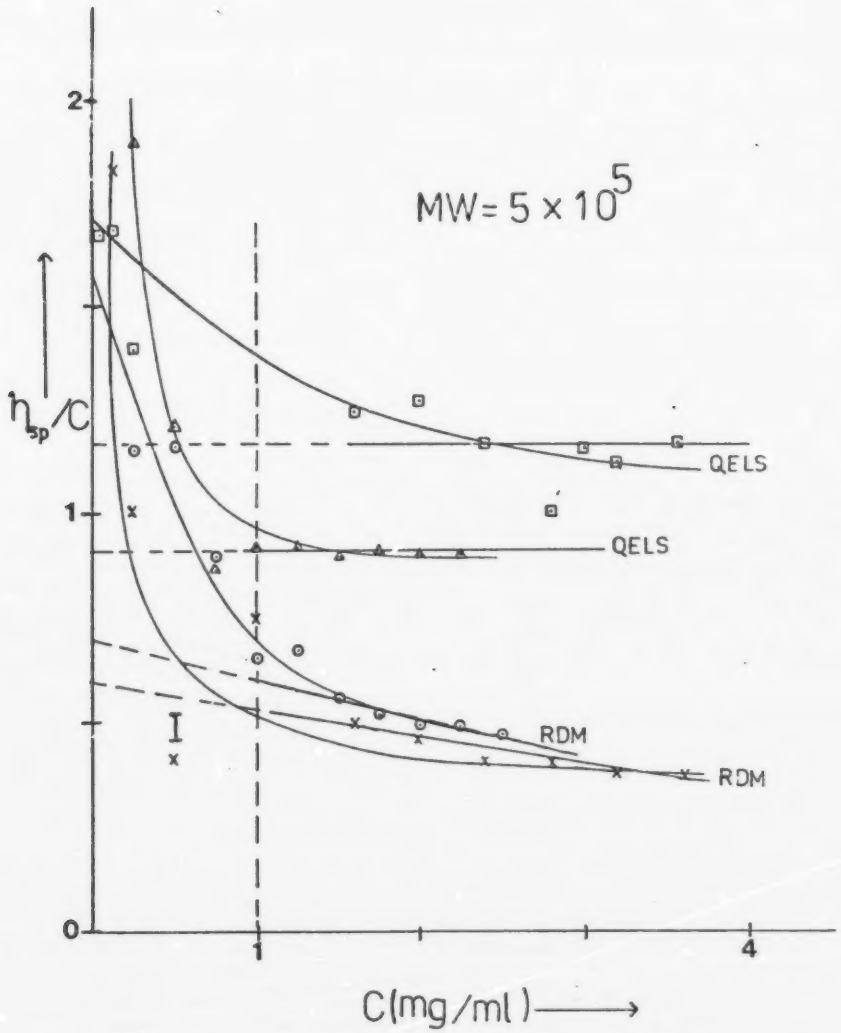
c is the polymer concentration.

The solution viscosity η was obtained by two methods:

i) By employing Stokes–Einstein's equation (Eqn. 4 Report 1) and using the measured diffusion coefficient of polystyrene latex spheres.

ii) By directly measuring the solution viscosity utilizing rotating drum viscosity method (RDM).

These measurements are shown in figures 5 and 6. The two methods yield different values for η. This can be attributed to the fact that the labelling QELS experiments sample a bulk solution viscosity at zero bulk shear. On the other hand RDM measurements are shear dependent. This again



Figures #5 and 6: Intrinsic viscosity determination:

Specific visocity measurements as a function of polyacrylamide concentration by employing QELS and RDM (Rotating Disk Method). It shows that the diffusing latex spheres through polyacrylamide matrix probe bulk viscosity at zero bulk shear, compared to the RDM measurements. Region marked I at c≤1 is considered to be anamalous region as the solution viscosities η, at low polymer concentrations tend to η_0 and since $\eta_{sp} = \frac{\eta-\eta_0}{\eta_0}$, it introduces large errors. Anamalous region divides the graph by dotted line at c=1. Thus the higher concentrations are extrapolated (dotted lines) to zero polymer concentration. The intercept provides intrinsic viscosity. The viscosities are in centipoise units.

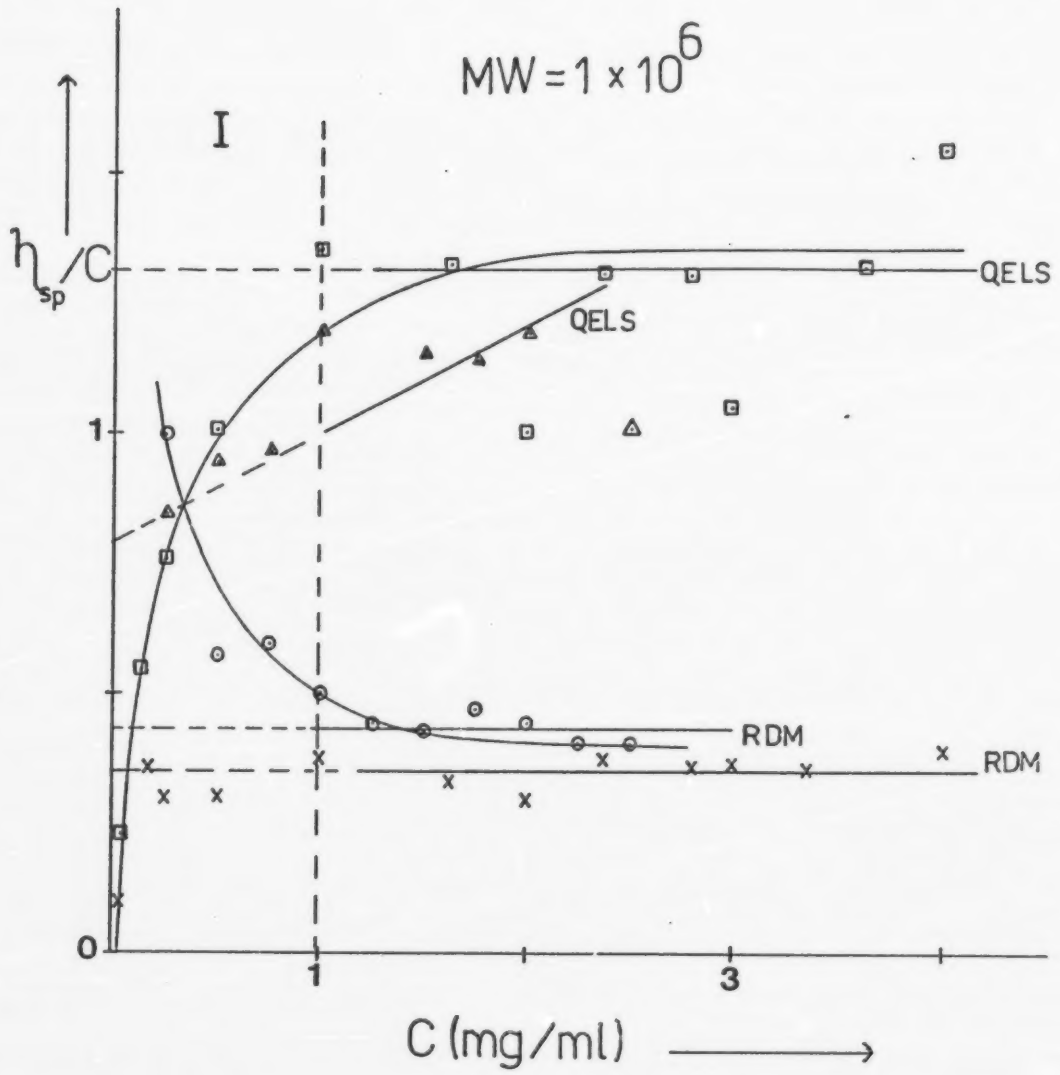


Figure #6: Intrinsic viscosity determination: See figure 5 for explanation.

proves the importance and potential of QELS technique.

The region marked "I" at a concentration of c ≤ 1.0 mg/ml on these graphs is considered to be an "Anamalous region" and it means that the solution viscosity η when approaches → η_o, pure solvent viscosity then at this concentration range we get erroneous values of $\frac{\eta_{sp}}{c}$ because η at c≤1.0 is very close to η and hence induces errors in $[\eta]$ determination. Since we are using spheres as a probe only and interested in polymer concentration therefore we extrapolate c>1.0 region to zero concentration to get intrinsic viscosity $[\eta]$. This anamalous region will disappear when the data is fit properly by computer. Furthermore, $[\eta]$ is proportional to the molecular weight, as

$$[\eta] = k M^{\alpha'} \qquad (4)$$

where k and α' are constants and M is the mol. wt. Figure 7 provides an α' value of 0.60, which confirms that the polyacrylamide system represents a non free draining random coil configuration which may act as a sphere which can be related to the radius of gyration. In order to obtain ν, the Simha's shape factor and k, the interaction parameter D/D_o should be least squared fit to the polynomial of equation. 1. This combined with a knowledge of degree of polymerization and volume fraction ϕ will yield a value for radius of gyration, and characteristic ratio. We haven't done this polynomial fit yet. Since we do not have sufficient range of polyacrylamide molecular weight as they are out of stock we are at present able to furnish results on two molecular weights only. Recently we got a range of molecular weight samples in polyethylene oxide and hoping to get some more of polyacrylamide samples. These and some experiments on coal and clay fines shall be concluded in next report. We are also planning to carry on a study

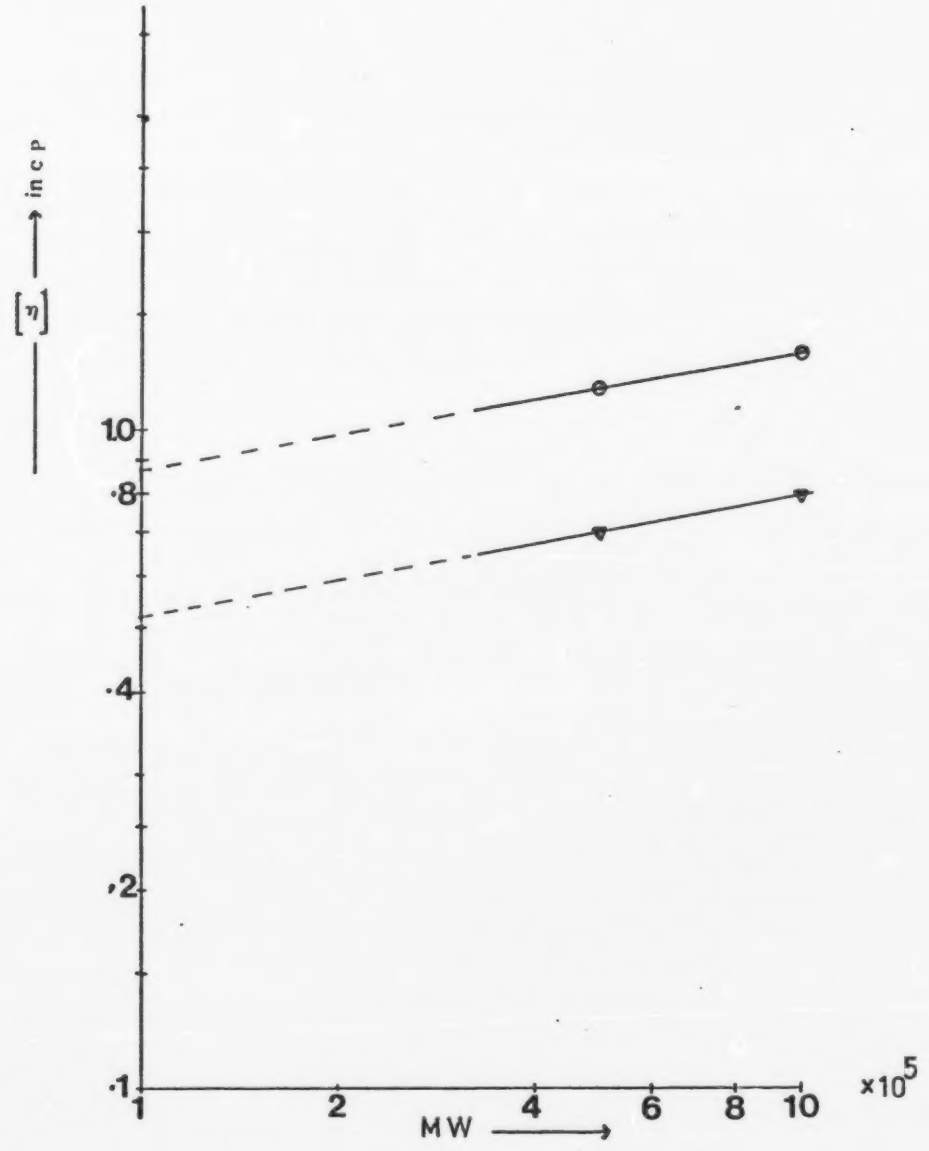


Figure #7: Confirmation analysis:

Intrinsic viscosity as a function of molecular weight of polyacrylamide. The log–log plot provides a slope of $\alpha'=0.60$, which shows that the polyacrylamide forms a non free draining random coil configuration in the aqueous solution.

of electrostatic interactions by monitoring the charge distribution of these flocullants. However the most important parameter which we obtained in this study to characterize polyacrylamide flocullant model system is the deducton of α' which shows a non free draining random coil polymer configuration.